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Influence of Heat Treatment on the Microstructure of $Fe_{70}Mo_5Cr_4Nb_6B_{15}$ Alloy

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The paper presents the results of microstructure and magnetic structure studies for amorphous $Fe_{70}Mo_5Cr_4Nb_6B_{15}$ alloy in the form of ribbons of about 20 μm in thickness. From X-ray diffraction and the Mössbauer spectroscopy the phase composition of the samples in the as-quenched state and after the thermal heat treatment are determined. From these studies it has been stated that the alloys in the as-quenched state are fully amorphous. X-ray diffraction studies show that in $Fe_{70}Mo_5Cr_4Nb_6B_{15}$ alloy subjected to the annealing at 800 K for 30 min the crystalline $Cr_{12}Fe_{36}Mo_{10}$ phase appears. Moreover, it has been found that the Mössbauer spectra of the alloys in the as-quenched state and after annealing in the wide temperature range has asymmetric doublets shape which is characteristic of paramagnetic materials. On the basis of the Mössbauer studies, it was found that the $Cr_{12}Fe_{36}Mo_{10}$ phase is a paramagnetic because in the Mössbauer spectrum of heat-treated samples there are no components from any ferromagnetic crystalline phase.

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1. Introduction

Amorphous alloys of the transition metals are a group of magnetic materials in which by appropriately selecting the chemical composition of the alloys can be obtained with interesting properties. Alloys with the Curie temperature near room temperature are particularly interesting because of the possibility of their use in magnetic refrigerators. The advantage of these materials is that a relatively low magnetic field strength is required for their re-magnetization.

A characteristic feature of amorphous alloys is the fluctuation of their density, resulting from the accidental arrangement of atoms [1, 2]. Depending on the chemical composition, various kinds of magnetic ordering may occur in Fe-based amorphous alloys [3]. It should be emphasized that within the same amorphous alloy there may also be present regions with so-called, medium-range ordering of atoms (MRO) [4]. Amorphous alloys are not temperature stable and through metastable states are striving for a crystalline state [5–7]. This process occurs as a result of structural relaxation, which occurs both during the production of amorphous alloys and during their heat treatment. Therefore, the microstructure and magnetic properties of amorphous alloys are affected not only by the chemical composition, but also by the conditions of their manufacture and heat treatment [4, 8, 9].

The aim of the study was to determine the effect of isothermal annealing the structure and microstructure of the amorphous $Fe_{70}Mo_5Cr_4Nb_6B_{15}$ alloy.

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2. Research material and research methodology

Studies were carried out on an $Fe_{70}Mo_5Cr_4Nb_6B_{15}$ alloy, which was produced by "melt-spinning" technique in the form of ribbons of 1 cm width and 20 μm thickness. Ingots of studied alloys of nominal compositions were produced by melting high-purity components in an induction furnace. Amorphous ribbons were obtained by rapid cooling of a molten material on a single rotating cylinder. The casting and melt-spinning processes were performed under a protective argon atmosphere. Heat treatment of the samples was carried out in a vacuum. The samples were placed in quartz tubes, which were pushed into the furnace preheated to the set temperature. After the sample reached a certain temperature, it was kept at this temperature for 30 min and then the sample and tube were pulled out and cooled in air. The accuracy of the temperature measurement was 1 K. The microstructure and structure of the samples were examined using a Mössbauer spectrometer and an X-ray diffractometer. The transmission Mössbauer spectra were measured at room temperature using conventional Mössbauer spectrometer working at a constant acceleration with a ^{57}Co(Rh) radioactive source of the 70 mCi in activity. Transmission Mössbauer spectra were measured both at room temperature and at the temperature of liquid nitrogen. X-ray diffraction was used to study the structure and phase composition of the samples. This measurement was carried out by means of a Bruker D8 Advance X-ray diffractometer with a copper anode.

3. Results and discussion

Figure 1 presents X-ray diffraction patterns obtained for the tested $Fe_{70}Mo_5Cr_4Nb_6B_{15}$ alloy samples.

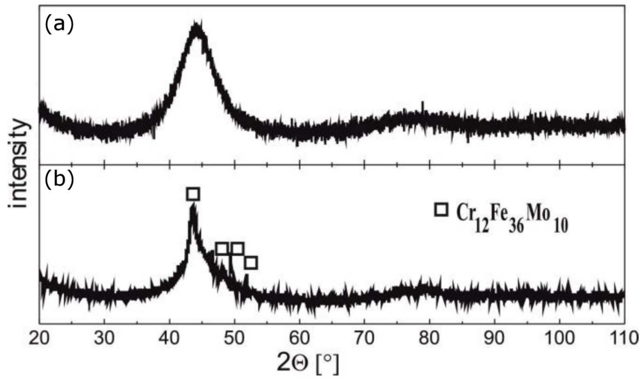

Fig. 1. X-ray diffraction patterns obtained for as-quenched $Fe_{70}Mo_5Cr_4Nb_6B_{15}$ alloy (a), and after heat treatment at 800 K for 30 min (b).

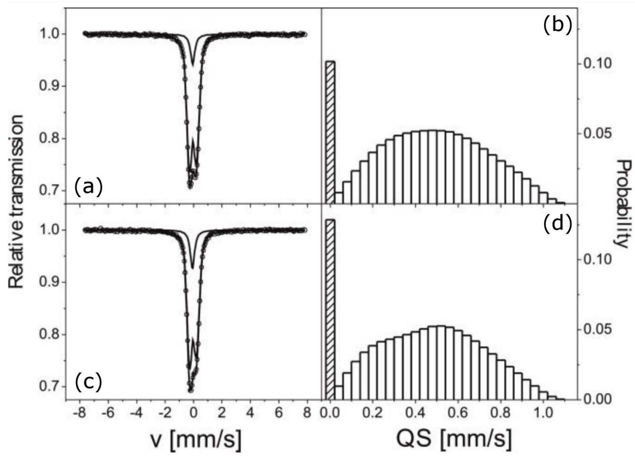

Fig. 2. Transmission Mössbauer spectra (a, c) and corresponding QS distributions (b, d) for the as-quenched $Fe_{70}Mo_5Cr_4Nb_6B_{15}$ alloy (a, b) and after heat treatment at temperature 800 K for 30 min (c, d), measured at room temperature.

The diffractogram obtained for the sample of the alloy in the state after solidification (Fig. 1a) shows a wide maximum occurring at an angle of $2\Theta \approx 44°$, which is characteristic of amorphous materials. The shape of the obtained diffractogram confirms the lack of translational symmetry and angular correlation in the spatial distribution of atoms. After heat treatment of the sample at temperature 800 K for 30 min, apart from wide maximum, a narrow maximum appears, indicating the presence of a crystalline phase in the alloy (Fig. 1b) [10]. Lack of translational symmetry and angular correlations in the distribution of atoms in amorphous alloys does not exclude the existence of clusters with different chemical compositions [11, 12]. The Mössbauer spectrometry is a good method for investigating such heterogeneities in amorphous alloys, because the local environment of the Mössbauer nuclei, in this case the ^{57}Fe nuclei, strongly influences the parameters of the hyperfine interaction. The transmission Mössbauer spectra of the obtained alloy, measured at room temperature, are shown in Fig. 2. The obtained spectra (Fig. 2a,c) are in the form of asymmetrical doublets and are characteristic for paramagnetic materials. In quadrupole splitting distributions $P(QS)$ (Fig. 2b,d), one can see that the probability is not equal to zero for $QS = 0$ [4, 13, 14].

Considering the shape of the quadrupole splitting distribution in which, apart from the non-zero probability for $QS = 0$, one wide maximum is visible, the best fitting of the Mössbauer spectrum for the as-quenched alloy is obtained when the spectrum is decomposed into a single line and a component with QS distribution. A single line can be assigned to areas with medium-range ordering of atoms with cubic symmetry [4, 15], without the magnetic ordering. As it is known, the cubic symmetry in the distribution of iron atoms leads to $QS = 0$ due to the "disappearing" of electric field gradient on the iron nuclei. It should be emphasized that in the Mössbauer spectrum, measured at room temperature, no Zeeman sextet is observed, which would come from areas with a magnetic ordering. The broad doublet may correspond to the amorphous regions in which the iron atoms have other non-magnetic atoms in their nearest neighborhood. In the case of a heat-treated alloy at the temperature of 800 K, a single line corresponds to areas with cubic symmetry, in which there is medium-range ordering of atoms and to the crystalline phase of $Cr_{12}Fe_{36}Mo_{10}$ — also with cubic symmetry (Fig. 2d). The $Cr_{12}Fe_{36}Mo_{10}$ phase must be a paramagnetic, because in the Mössbauer spectra of the heat-treated alloy samples there are no components derived from any ferromagnetic crystalline phase. The Mössbauer spectroscopy studies were also carried out at the temperature of liquid nitrogen.

Figure 3 shows the Mössbauer spectrum recorded for measured alloys at the temperature 77 K. The spectrum of this sample was fitted with a single line and the Zeeman sextet. With the hyperfine field induction distributions, a linear dependence of the isomeric shift on the

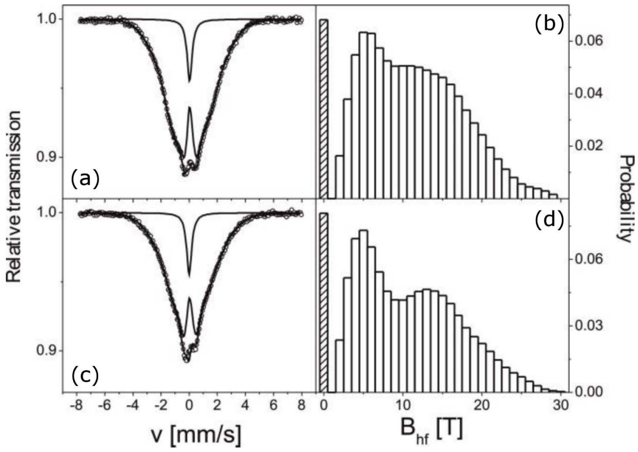

Fig. 3. Transmission Mössbauer spectra for the as-quenched $Fe_{70}Mo_5Cr_4Nb_6B_{15}$ alloy (a) and after heat treatment at 800 K for 30 min (c), measured at the temperature of liquid nitrogen (77 K), and hyperfine field induction distributions obtained from them (b,d).

hyperfine field induction was assumed. The same applies to the spectrum recorded for a sample of an alloy subjected to annealing. In this case, the spectrum can also be fitted with sextet with overlapping lines and a single line. This indicates that the cubic symmetry areas appearing in the sample are not superparamagnetic particles [4, 16].

Fundamental fitted hyperfine parameters obtained from the analysis of the Mössbauer spectra, measured at room temperature and temperature of liquid nitrogen, for the as-quenched $Fe_{70}Mo_5Cr_4Nb_6B_{15}$ alloy and after heat treatment are listed in Table I.

TABLE I

Fitted hyperfine parameters of the spectra decomposition, measured at the room temperature (308 K) and at the temperature of liquid nitrogen (77 K), shown in Figs. 2,3, for the $Fe_{70}Mo_5Cr_4Nb_6B_{15}$ alloy in the as-quenched state and after annealing at 800 K for 30 min: the mean value of the quadrupole splitting (QS), the average value of the hyperfine field induction (B_{hf}), percentage share of individual components in the spectrum: single line (I_{SL}), the relative area of the doublet (I_{QS}), the relative area of the amorphous ferromagnetic component (I_{am}).

Heat treatment and temperature of measurement	QS [mm/s]	I_{QS} [%]	I_{SL} [%]	B_{hf} [T]	I_{am} [%]
as-quenched state in 308 K	0.50±0.05	90	10	–	–
as-quenched state in 77 K	–	–	7	11 ± 1	93
after annealing in 308 K	0.49 ± 0.05	87	13	–	–
after annealing in 77 K	–	–	8	11 ± 1	92

Sextet with wide overlapping lines, which corresponds to the average hyperfine field induction $B_{hf} = 11$ T, comes from the ferromagnetic amorphous phase. A single line, just like at room temperature, can be assigned to areas in which there is medium-range ordering of atoms with very low iron content. After heat treatment, the contribution of the paramagnetic phase in the sample decreases, as evidenced by the reduction in the percentage of I_{QS}. This is accompanied by an increase in the share of a single line in the spectrum.

4. Conclusion

Using the melt spinning method, amorphous $Fe_{70}Mo_5Cr_4Nb_6B_{15}$ alloy in the form of ribbons were produced. After heat treatment of the alloy, the presence of a crystalline phase was found on the basis of X-ray diffraction studies.

In the case of the tested alloy both in the as-quenched state and after heat treatment in the quadrupole splitting distribution, a non-zero probability for $QS = 0$ is observed. This indicates the existence of areas with cubic symmetry in the distribution of iron atoms.

After the heat treatment of the $Fe_{70}Mo_5Cr_4Nb_6B_{15}$ alloy, at 800 K for 30 min, the crystalline phase $Cr_{12}Fe_{36}Mo_{10}$ with cubic symmetry appears. Based on the obtained results, it was found that the $Cr_{12}Fe_{36}Mo_{10}$ phase is a paramagnetic phase.

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